



## Short communication

Stability of trimethyl phosphate non-flammable based electrolyte on the high voltage cathode ( $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ )

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## H I G H L I G H T S

- TMP based electrolyte has a high capacity retention in the battery with LMN cathode.
- Using this electrolyte, the gas generation was suppressed inside the battery.
- A film with cross-linked structure was formed on the cathode after cycles.
- This film became a passivation film to suppress the TMP decomposition.

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## A B S T R A C T

Trimethyl phosphate (TMP) which is a non-flammable solvent is a good candidate to replace flammable carbonates in battery electrolytes. In the case of Li-ion battery using high voltage cathode such as  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNM), the use of TMP based electrolyte leads to high cycle performance (96% capacity retention after 50 cycles). Also gas generation drastically decreased. According to careful observation of the LNM surface by scanning electron microscopy (SEM) after cycles, it has been found that TMP decomposes itself and forms polymer based film on the electrode surface suppressing further electrolyte decomposition. This work leads us to propose new electrolytes for Li-ion batteries using high voltage cathode.

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## 1. Introduction

Li-ion Battery (LIB) with higher energy density has been widely developed for electric vehicle to drive longer-distance [1,2]. One way to meet this objective is using a high voltage cathode such as  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  (LNM) [3–10]. However such LIB has a significant problem of electrolyte decomposition at high voltage, leading to gas generation. Therefore, remarkably stable electrolyte on the cathode is required.

In order to suppress electrolyte decomposition at high voltage, it has been suggested to coat the cathode with a protective film. Conventional electrolytes like ethylene carbonate (EC) and diethyl carbonate (DEC) cannot form such a passivation film in this case. Some research institution has tried to develop a new additive to make a protective film electrochemically [11], but efficient one has not been found up to now. Fluorinated carbonates have also been studied in replacement of carbonates but corresponding electrolytes present high resistance and need to be mixed with carbonates in order to reach acceptable solubility of lithium salt. Moreover their mixture with conventional carbonates based electrolyte is needed to obtain good cycle performance and the problem of gas generation still remains.

In our paper, instead of conventional electrolyte, pure phosphate based electrolyte, in particular TMP, was used because it is known to be a non-flammable solvent and have good solubility of lithium salt. The cell with TMP based electrolyte showed a good

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capacity retention after 50 cycles. And the electrolyte was able to suppress the gas generation. In addition, it was found that TMP based electrolyte was stable in lithium ion battery with high voltage cathode. We succeeded to propose a new electrolyte for the cell with high voltage cathode.

## 2. Experimental

Performances of batteries such as first charge–discharge curve and cycle life were performed by using coin cells. Solvents (TMP, EC and DEC) and lithium hexafluorophosphate ( $\text{LiPF}_6$ ) were purchased from Sigma–Aldrich Co. LLC. And polyolefine based separator was obtained from Celgard®, Inc. Coin cells were assembled using  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  as a cathode material and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  (LTO) as an anode material. In this report, LTO electrode which intercalates lithium ion at 1.5 V vs  $\text{Li}/\text{Li}^+$  was selected because it was known that TMP based electrolyte was unstable below 1.0 V vs  $\text{Li}/\text{Li}^+$  [12–14].

The cells was charged at constant current (0.1 C-rate) until 3.75 V and the cut-off voltage of discharge was 2.0 V. All evaluations were performed at 20 °C. Electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range from 100 KHz to 100 mHz. The ac amplitude was 10 mV. The impedance was measured after 3 cycles and at different state of charge (SOC).

Gas analysis was carried out *in situ* and *in operando* to determine the nature of decomposition products from electrolytes and the amount of generated gas. El-cell® equipped with gas outlet was prepared. This cell was directly connected to mass spectrometer (MS) to detect *in operando* gaseous products during first charge and floating at 3.75 V.

Linear sweep voltammetry (LSV) using three electrode cell with platinum as working electrode and counter electrode and lithium as reference was performed on 2 ml of electrolyte in order to check the stability of electrolyte at high voltage. The electrochemical test was performed between 3.0 and 6.0 V vs  $\text{Li}/\text{Li}^+$ .

The morphology of surface and components on the LNM cathode after cycles were analyzed by SEM and XPS measurements. For SEM and XPS measurement, the cathode was taken out from the coin cell after cycles in the glove box under Ar atmosphere. Before measurement, the cathode was washed 3 times by dipping into DMC for 10 min and dried under vacuum. Then it was transferred to SEM and XPS equipment without exposing to atmosphere.

## 3. Result and discussion

### 3.1. Electrochemical window of electrolyte

TMP based electrolyte was unstable at high voltage as shown by the onset voltage of electrochemical oxidation at around 3.8 V vs  $\text{Li}/\text{Li}^+$  (Fig. 1). This voltage was lower than that of EC:DEC based electrolyte which was around 4.6 V vs  $\text{Li}/\text{Li}^+$ . Based on this observation, it is expected that TMP will be decomposed before EC:DEC in the cell.

### 3.2. Chronopotentiometry and EIS

Fig. 2 shows the first charge–discharge curve. High capacity was obtained in the first charge–discharge process evaluated by chronopotentiometry technique in coin cell composed of LNM and LTO electrodes even if TMP based electrolyte was unstable at high voltage (Fig. 2). The efficiency of first charge–discharge was 92%, which is similar to that of EC:DEC based electrolyte (93%). In addition, the discharge capacity was almost same ( $134 \text{ mAh g}^{-1}$ ) as that of EC:DEC based electrolyte ( $137 \text{ mAh g}^{-1}$ ). Moreover the charge–discharge curve indicated that there is no phenomenon attributed to side reaction such as electrolyte decomposition.

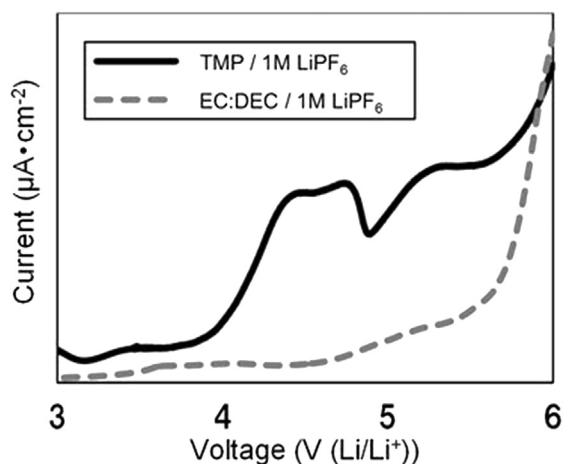


Fig. 1. LSV measurement ( $10 \text{ mV s}^{-1}$ ) using platinum as a working and a counter electrode, lithium as a reference electrode.

Compared to EC:DEC based electrolyte, the charge–discharge capacity was lower in the TMP based electrolyte due to higher viscosity and poor wettability of the separator.

The electrochemical impedance spectrum of the cells are shown in Fig. 3. The impedance was measured after 3 cycles and at 0, 50, 100% SOC. The semicircle in the high to intermediate frequency range seems to be attributed to the impedance of surface film with a contribution from charge-transfer resistance. For the TMP based electrolyte, this resistance was higher than that of EC:DEC based electrolyte. From these results, it is considered that the resistance of film derived from the decomposition of TMP is higher.

### 3.3. Cycle performance

Fig. 4 shows the cycle performance using TMP based electrolyte or EC:DEC based electrolyte. For the TMP based electrolyte, 96% capacity retention was observed after 50 cycles, which is similar to using EC:DEC based electrolyte (92%). This cell with TMP based electrolyte shows an excellent cycle performance, with no capacity fade during cycles. This result clearly shows that TMP based electrolyte, although it is electrochemically unstable as Fig. 1 shows, is a suitable electrolyte for the cell with high voltage cathode.

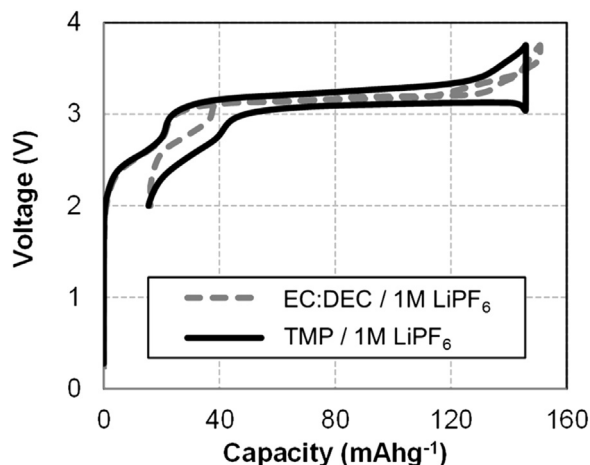


Fig. 2. First charge–discharge curve using TMP/1 M  $\text{LiPF}_6$  or EC:DEC/1 M  $\text{LiPF}_6$  at 20 °C and C/10 rate.

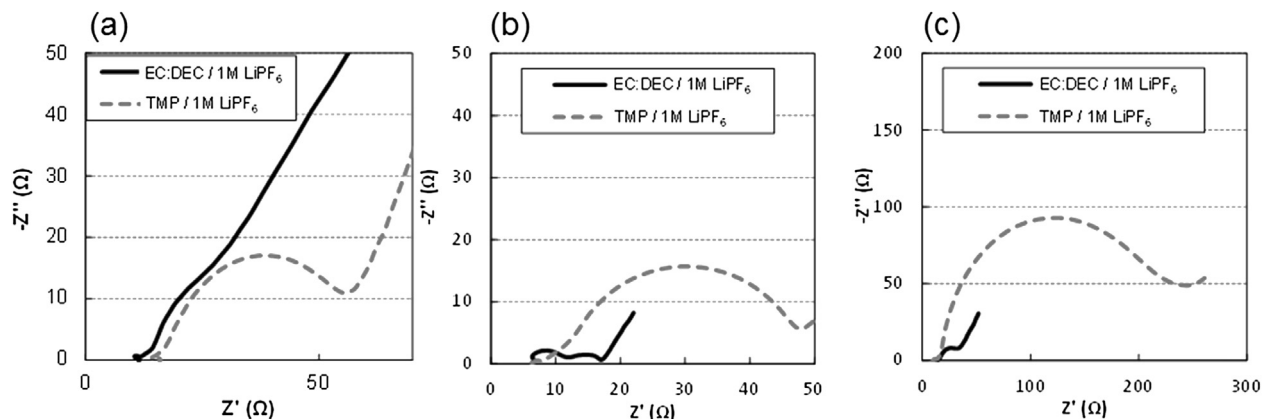


Fig. 3. Impedance spectroscopy in LNM/LTO cells at different SOC ((a)0%, (b)50%, (c)100%).

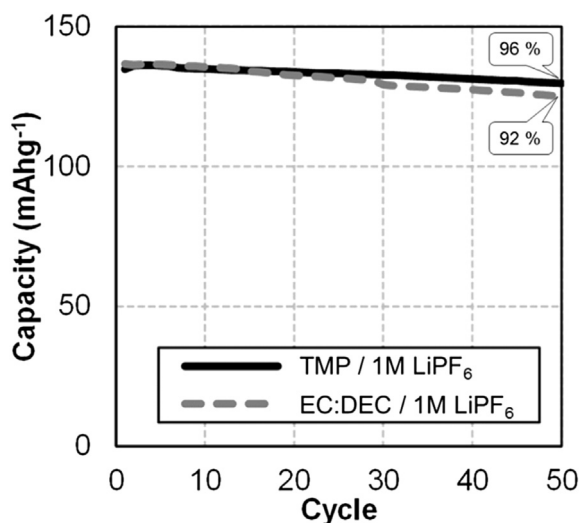


Fig. 4. Cycle performance using TMP/1 M LiPF<sub>6</sub> and EC:DEC/1 M LiPF<sub>6</sub> at 0.1 C (25 °C).

#### 3.4. Analysis on the cathode surface

The use of TMP based electrolyte accomplished the high capacity retention in the cell using LNM cathode, although this electrolyte was unstable at high voltage. Here, in order to understand this phenomena, the surface on the cathode after cycles was observed by SEM measurement. SEM image shows that a film with networked structure was clearly observed for the TMP based electrolyte (Fig. 5(a)) And this film covered the surface of the LNM

active material. The film is probably comes from the polymerization or oligomerization of TMP. Similar result was observed when EC mixed electrolyte was used at a previous paper [15]. The paper said that EC oxidatively decomposes on the LNM cathode and makes a film by polymerization. This film prevents TMP from the further decomposition. As results, it leads to good cycle performance. Moreover, a partial and thin film was observed on the surface of the active material when EC:DEC based electrolyte was used (Fig. 5(b)). It can be seen that the cycle performance for the EC:DEC based electrolyte is worse because the film was not efficient to prevent EC:DEC from the decomposition on the cathode.

#### 3.5. Gas analysis

In order to determine the nature of decomposition product, gas analysis was carried out during first charge and floating step. For the TMP based electrolyte, not so many components were detected. The main gas was argon (Fig. 6(a)), which comes from the assembling process in the glovebox. Formation of CH<sub>4</sub> and CO was based on the decomposition of TMP. However, their amounts were lower than those of EC:DEC based electrolyte (Fig. 6(b)). Surprisingly, no phosphorus fragment was observed in this measurement. Therefore, it could be said that the decomposition of TMP on the LNM cathode did not to occur. The amount of H<sub>2</sub> and O<sub>2</sub> gas during first charge and floating process was very low, and the amount of gas generation was constant during the floating at 3.75 V (Fig. 7(a) and (b)). On the other hand, for the EC:DEC based electrolyte, many peaks derived from the decomposition of DEC were detected (Fig. 6(b)). Consequently, DEC is mainly decomposed on the LNM cathode, and generated large quantities of gas. The amount of H<sub>2</sub> and O<sub>2</sub> gas increased as the cell voltage became higher during first

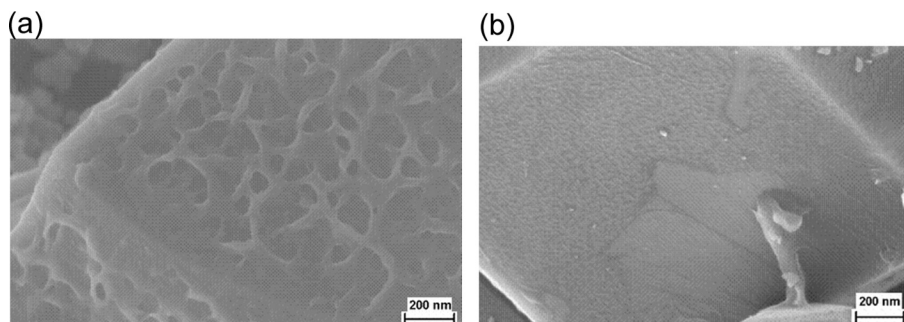


Fig. 5. SEM image on the cathode after 50 cycles using (a) TMP/1 M LiPF<sub>6</sub> and (b) EC:DEC/1 M LiPF<sub>6</sub>.

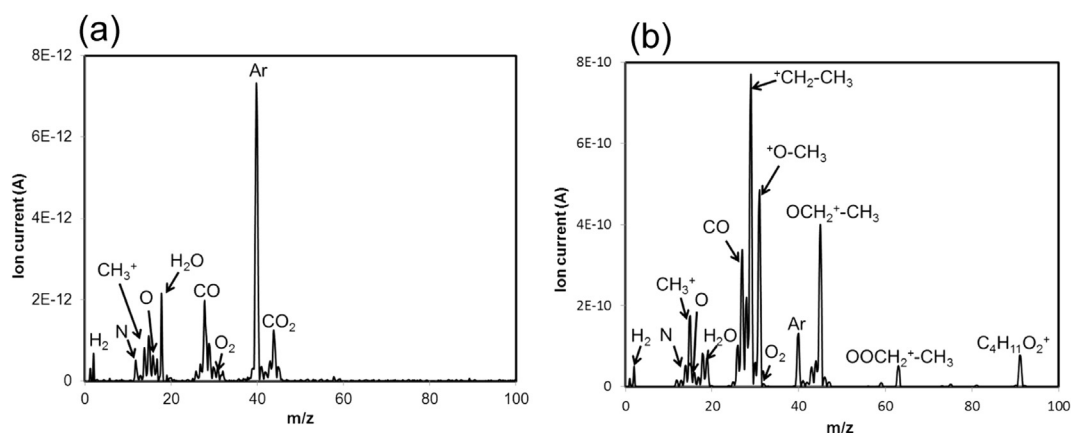


Fig. 6. Gas component after first charge and float for 5 h at 3.75 V in (a) TMP based electrolyte and (b) EC:DEC based electrolyte.

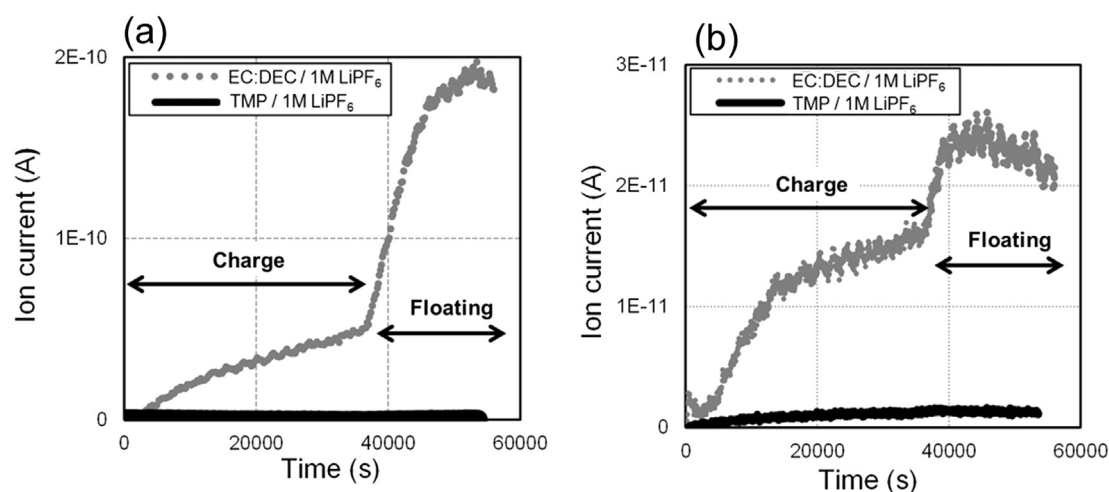


Fig. 7. Gas generation of (a)  $H_2$  and (b)  $O_2$  during first charge at 0.1 C and floating at 3.75 V.

charge (Fig. 7(a) and (b)) gas is still generated during floating process.

### 3.6. XPS characterization

In order to reveal the nature of the component of the film formed on the LNM cathode after cycles, XPS measurements were

carried out.  $C_{1s}$  and  $P_{2p}$  peaks correspond to C–O bond and P–O bond in TMP based electrolyte (Fig. 8). No lithium component was detected (Data was not shown). As a result, these peaks seem not to be the decomposition of lithium salt but the decomposition of TMP. And this decomposition product of TMP forms a C–O and P–O bond containing film. On the other hand, for the EC:DEC based electrolyte, from the spectra of  $C_{1s}$ , C=O component was detected, which

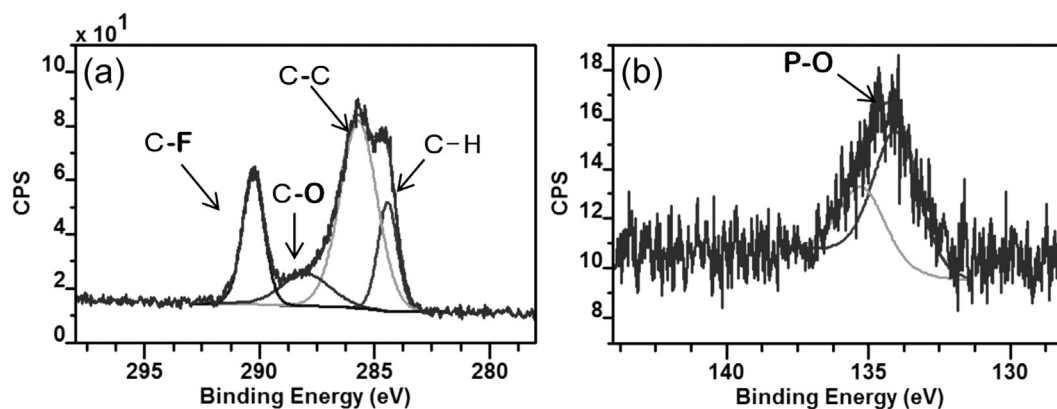


Fig. 8. (a)  $C_{1s}$  and (b)  $P_{2p}$  XPS core peak on cathode electrode after 15 cycles in TMP based electrolyte.

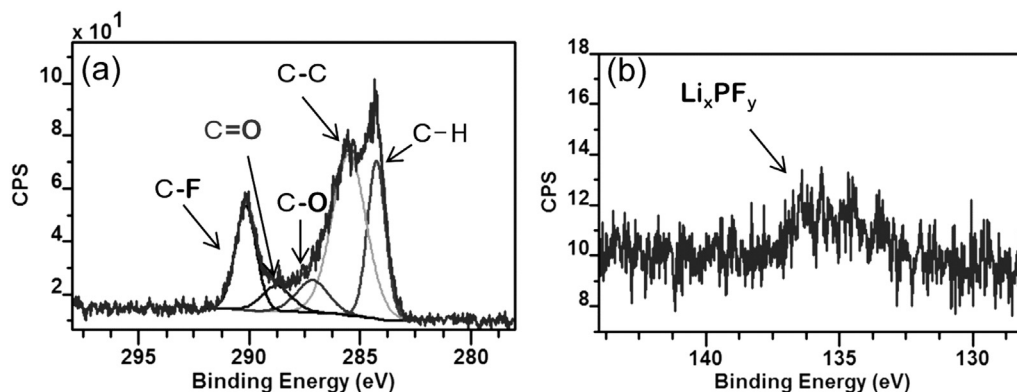


Fig. 9. (a) C1s and (b) P<sub>2p</sub> XPS core peak on cathode electrode after 15 cycles in EC:DEC based electrolyte.

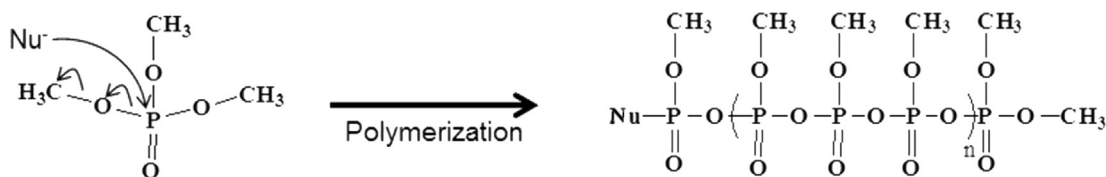


Fig. 10. Film formation mechanism of TMP based electrolyte on the cathode.

is attributed to the peak of the decomposition of DEC (Fig. 9(a)). In the P<sub>2p</sub> spectra, a peak at 137 eV corresponding to the Li<sub>x</sub>PF<sub>y</sub> component was detected (Fig. 9(b)). It means that not only EC:DEC electrolyte but also lithium salt decompose on the LNM cathode. And the decomposition product seems to form a film as previous report said [15].

## 4. Discussion

### 4.1. Mechanism of film formation

It was demonstrated that TMP decomposed on the LNM cathode at high voltage and the decomposition product became a film with networked structure to prevent TMP from further decomposition. TMP based electrolyte leads to polymer film on the LNM electrode during cycles. This result was similar to that observed in EC based electrolyte [12,15–18]. XPS showed that this film is constituted by P–O and C–O bond. Moreover, a small amount of CH<sub>3</sub><sup>+</sup> and O<sub>2</sub> gas was detected in MS measurement during first cycle. From these results, we could propose as a mechanism the nucleophilic moieties like fluoride ion (F<sup>−</sup>) or alkoxide ion (CH<sub>3</sub>O<sup>−</sup>) attacks phosphorus atom located in the center of TMP molecule and producing a fragment which can react with another TMP molecule. Finally this chain reaction could happen successively and leads to the formation of polymer or oligomer film as shown in Fig. 10.

## 5. Conclusion

TMP based electrolyte is suitable as an electrolyte for the cell with high voltage cathode such as LNM. The cell with this

electrolyte shows a good capacity retention after 50 cycles. From SEM image on the LNM surface after cycles, a polymer film derived from oxidative decomposition of TMP was formed. This film suppressed the further decomposition of TMP. As results, TMP based electrolyte is stable on the LNM cathode when charged at high voltage. These results clearly demonstrate that TMP based electrolyte is an attractive electrolyte for the cell with LNM cathode.

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